

Recent Developments on Autonomous Corrosion Protection through Encapsulation

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ABSTRACT

This paper concerns recent progress in the development of a multifunctional smart coating, based on microencapsulation, for the autonomous detection and control of corrosion. Microencapsulation has been validated and optimized to incorporate desired corrosion control functionalities, such as early corrosion detection and inhibition, through corrosion-initiated release of corrosion indicators and inhibitors, as well as self-healing agent release triggered by mechanical damage.

While proof-of-concept results have been previously reported, more recent research and development efforts have concentrated on improving coating compatibility and synthesis procedure scalability, with a targeted goal of obtaining easily dispersible pigment-grade type microencapsulated materials. The recent progress has resulted in the development of pH-sensitive microparticles as a corrosion-triggered delivery system for corrosion indicators and inhibitors. The synthesis and early corrosion indication results obtained with coating formulations that incorporate these microparticles are reported. The early corrosion indicating results were obtained with color changing and with fluorescent indicators.

INTRODUCTION

The development of a smart multifunctional corrosion-protective coating system, based on a pH-sensitive delivery system, has evolved significantly over the last few years [1-4]. This effort has resulted in a coating that incorporates pH-sensitive microcapsules with a core that can incorporate corrosion indicators, corrosion inhibitors, and self-healing agents to achieve the desired functionalities of early corrosion detection, controlled release of corrosion inhibitor(s), and self-healing of mechanical damage. Each function represents one important research area in recent corrosion protective coatings development: corrosion-controlled delivery systems, corrosion sensing coatings, and self-healing coatings.

The need for environmental compliance in corrosion control, very specifically, hexavalent chromium replacement, has motivated recent intense research and development efforts to focus on new corrosion inhibitors and coating formulations to incorporate these new inhibitors. As a result, new and old corrosion inhibitors have been tested and evaluated for corrosion protective coating applications. As challenging as it is to find a new corrosion inhibitor that comes close to hexavalent chromium in corrosion inhibition efficiency, it has been equally challenging to develop a pigment-grade product that is compatible with coating formulations based on new inhibitor chemistries. Achieving coating compatibility can be a challenge with a new corrosion inhibitor when: (1) the water solubility of the inhibitor is too high, (2) the inhibitor is too reactive thus not stable in the presence of other coating components, and (3) has other negative effects on the paint formulation that affect storage, application, curing or use, and emulsion stability. To overcome the coating compatibility challenge, the development

of an inhibitor delivery system is often necessary. While controlled delivery concepts and systems were used in pharmaceutical and agricultural applications initially, there has been a wide range of delivery systems tailored for surface coatings and corrosion inhibitors in recent years [5].

Early corrosion sensing and detecting coatings have been an area of research interest due, at least in part, to some corrosion related catastrophic failures such as those involving aged aircraft. The failures often were the result of the sudden fracture of high strength aluminum alloys caused by localized corrosion, which can be easily overlooked using traditional and most often used visual inspection techniques. Other incidents involve new coating products that are often developed to address environmental compliance and economic factors. These coatings sometimes fail earlier than expected due to the fact that there is no correlation between the specified accelerated and/or laboratory corrosion tests and actual field performance. These incidents highlight the need for early corrosion detection technology, especially for corrosion in recessed/hidden areas. Besides safety concerns, another obvious benefit for early corrosion detection and hidden corrosion detection is economic impact. When detected early, coating and corrosion damage require minor repair at a lower cost compared to the high expense of a major structural overhaul. The cost difference can be enormous. While damage detection sensors and tools are being developed to aid corrosion inspection, a protective coating with an integrated corrosion sensing function is highly desirable. Earlier research in corrosion sensing paints involved the incorporation of corrosion sensing compounds directly into the paints [6-9]. More recent efforts involved corrosion indicators with higher detection sensitivity [10,11] and different delivery systems to overcome coating incompatibilities [12,13].

Self-healing materials have been a recent and rapidly growing field of research. The initial research that targeted composites [14] has subsequently spread into other areas [15-21]. Research in self-healing polymer coatings, as a subset of self-healing polymers, includes two approaches: built-in structures that provide healing functions [14, 22] and polymer chemistries that provide intrinsic self-healing [23-25].

Our research on smart coatings for corrosion management applications has evolved from the earlier efforts to develop pH-sensitive microcapsules to incorporate the functions of indication, inhibition, and self-healing into a smart coating, to more recent efforts to tailor and fine-tune the microencapsulation system for each function. New delivery systems, such as organic microparticle formulations for indicators and inhibitors, elongated microcapsules for self-healing, as well as new self-healing chemistries and inorganic delivery systems are currently under development, evaluation, and optimization. These newer delivery systems are being developed as pigment-grade materials to be easily incorporated into paint formulations that are targeted towards several commercial applications.

This paper concerns the most recent progress from our efforts in synthesizing pigment-grade pH-sensitive microparticles as a delivery system for corrosion indicators and inhibitors and selected test results on the corrosion sensing function.

PH-SENSITIVE MICROPARTICLE SYNTHESIS

As a result of the initial development efforts on a pH-sensitive delivery system [1], it was concluded that the requirements for all three functions would be different depending on the coating system, coating type and ratios of desired functions. While larger size self-healing microcapsules that contain liquid film-forming agents are needed for effective healing agent delivery at each damage site [26], there is no benefit in having a larger size for corrosion indicator or inhibitor delivering microcapsules. On the contrary, large microcapsules are more likely to break during coating mixing and application and more likely to cause coating defects. The desired size for a pigment-grade microcapsule is from sub-microns to a few microns. As a result, indicator and inhibitor microcapsules have been optimized to obtain smaller sizes, better mechanical properties of the capsule walls, and a final product in free flowing powder form [2-4].

During the microcapsule optimization process for indicator and inhibitor delivery, it was recognized that for solid corrosion inhibitors, especially organic corrosion inhibitors and practically all corrosion indicators, it is often possible to incorporate the active ingredients into pH-sensitive microparticles instead. The initial motivation was to achieve higher active ingredient loading using a particle formulation with no solvent in the final product [12]. The newly developed microparticle formulation has the following additional benefits: (1) low energy requirement for the encapsulation process: only a low mixing speed is required for very small size particle formation, compared with the high shear energy needed for small microcapsule formulation; (2) elimination of the mechanical strength requirement for the delivery system: if the microparticles are mechanically broken during paint mixing and application, this will only result in particles smaller than their original with no premature content release as with the microcapsule formulations; (3) easy processing and scalability to achieve pigment characteristics and grade final product: it is easier to separate, wash, and spray dry the microparticle formulation to get a free flowing powder and the process is easier to scale-up. These are important attributes for commercial applications.

Microparticle Synthesis Process

A representative microparticle synthesis process is shown Figure 1. The two phases involved are the water phase and the solvent phase. The water phase contains the pre-polymer for particle formation and the surfactants. The solvent phase contains a water-miscible solvent with active ingredient. In the case of an inhibitor particle, the synthesis process includes dissolving the inhibitor into a water miscible solvent, such as ethanol or isopropanol, first. The inhibitor solution is then added to a continuous water phase. This process allows the inhibitor to be incorporated into the particle rather than being dissolved into the water. While the process is not completely understood, it involves a somewhat spontaneous micro-emulsion process, similar to the Ouzo Effect, but less stable by which the inhibitor solution is dispersed into droplets. The polymerization reaction then occurs at the interfaces of these droplets which cause the inhibitor to be incorporated into particles before being dissolved into the water. Surfactants are used to control size and maintain particle distribution. A similar process is used to synthesize corrosion indicator microparticles.

A typical formula for pH sensitive microparticles with incorporated corrosion indicator is shown in Table 1. SEM micrographs of pH indicator containing particles are shown in Figure 2.

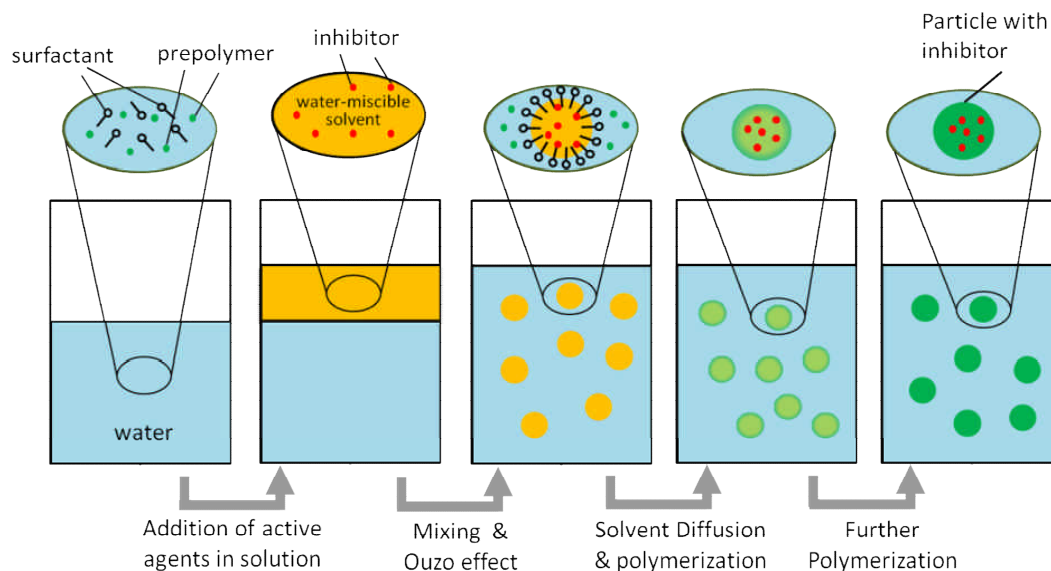


Figure 1. Microparticle Formation Process.

Table 1. Microparticle formula with incorporated corrosion indicator.

Reagent	Mass (g)
Water	900
Melamine	45
formaldehyde (37%)	96
Crosslinker	32.5
Surfactant	6
Indicator	50
Solvent	133
Catalyst	
Acid	to pH 5.5

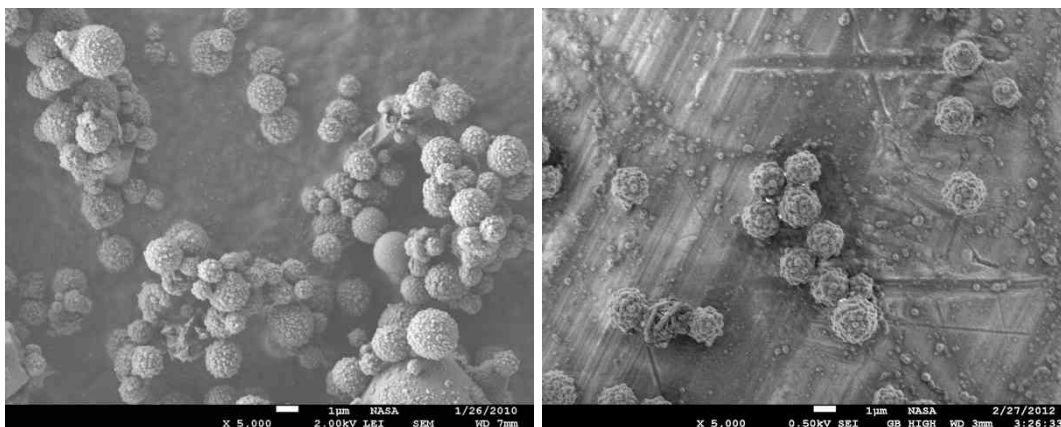


Figure 2. SEM image of indicator microparticles with color changing indicator phenolphthalein (left) and with fluorescent indicator fluorescein (right)

CORROSION SENSING COATING FORMULATIONS

Two corrosion sensing coating formulations are reported in this section: one that contains phenolphthalein, a pH indicator which indicates corrosion with a visible color change, and a second that contains a corrosion indicator, which is a pH corrosion indicator through fluorescent changes, fluorescein.

Corrosion Sensing Coating with Colour Changing Indicator

For color changing corrosion sensing coating, encapsulated phenolphthalein was incorporated into a commercially available solvent-based 3k acrylic-urethane clear coat coating and its effectiveness in early corrosion indication, as well as detection of hidden corrosion, was demonstrated experimentally. Detailed information of the test results follow.

Figure 3 shows the results from a salt immersion test of steel panels coated with a clear urethane coating blended with 10 weight% of phenolphthalein microparticles. The panels were scribed and observed for visually detectable changes versus exposure time. Repeat observations confirmed that

the onset of corrosion was visible in the scribe in less than 60 seconds after immersion, which is considerably earlier than the 2 hours it takes for the typical color of rust to appear.

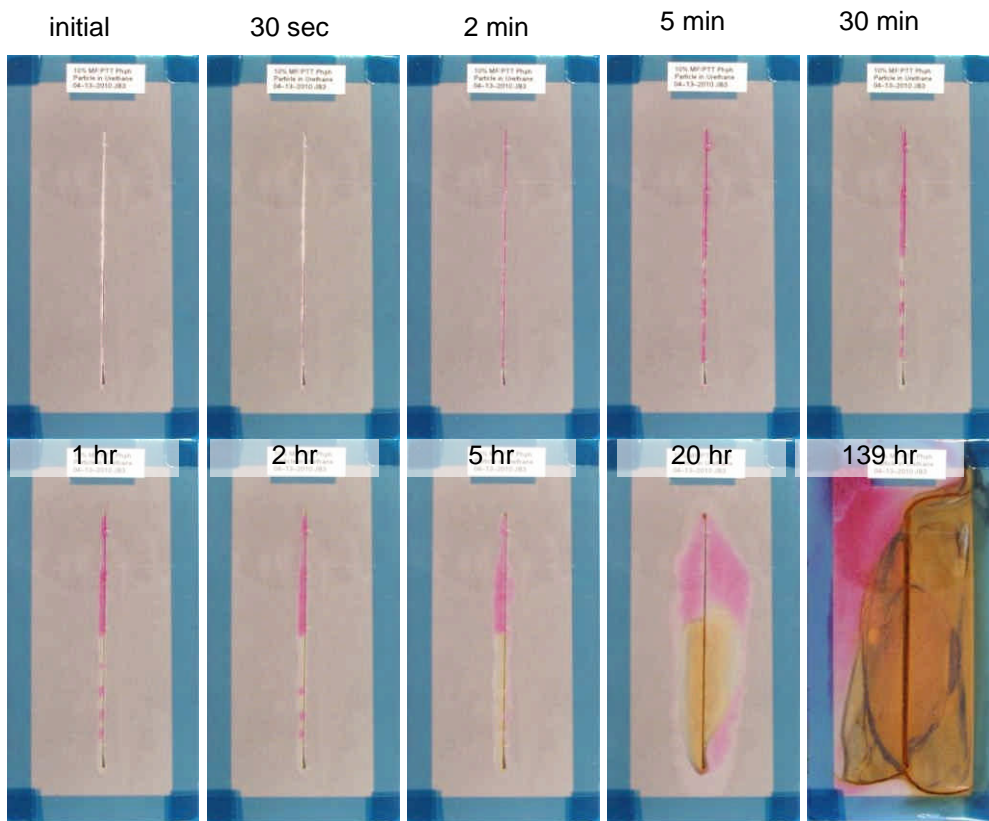


Figure 3. Corrosion indication test results.

In addition to early corrosion detection, another potential application of the smart coating is to detect hidden corrosion. A conceptual illustration of how these coatings can be used to detect hidden corrosion on structural bolts is shown in Figure 4, on the left. Bolts tend to corrode on the hidden shaft area in advance of the visible corrosion detected on the bolt head or nut. Often, the head and nut are in pristine condition, even when significant corrosion has occurred on the shaft. There is no method to identify the degree of corrosion without removing the bolt from service. A coating that changes color on the bolt head or nut when corrosion starts would greatly enhance the inspection process and increase the safety and reliability of the structure.

An experiment was designed to test the effectiveness of the encapsulated indicator to detect hidden corrosion when incorporated into a coating system. Several coating systems were prepared in order to find a coating system that would indicate crevice corrosion, as can be expected to occur in a nut and bolt assembly designed to duplicate the use of bolts to hold a structure. Some coating systems demonstrated the ability of the coating to indicate hidden corrosion as evidenced by the appearance of a purple color after 600 hours of salt fog exposure (Figure 4, on the right).

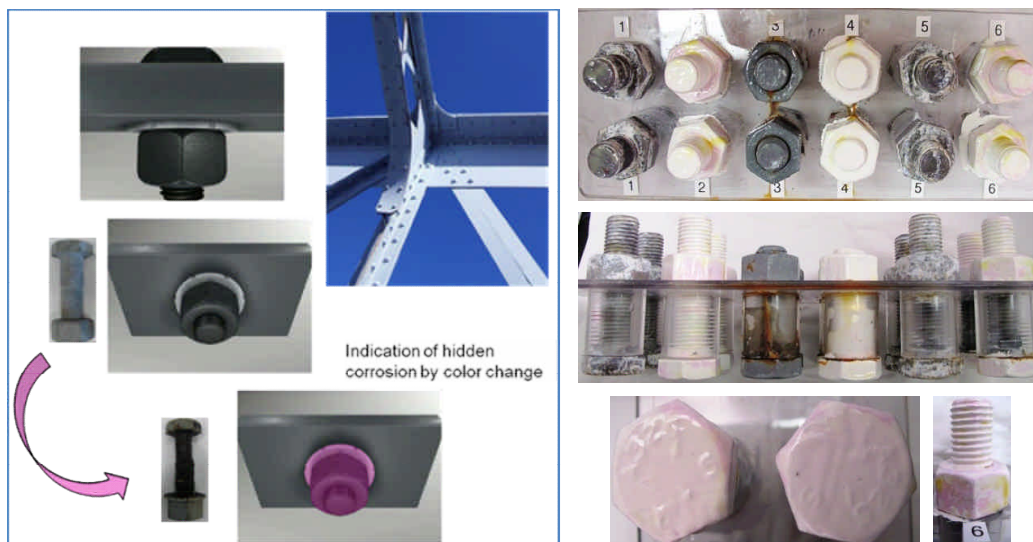


Figure 4. Conceptual illustration of hidden corrosion indication in structural bolts (left). Indication of hidden corrosion after 600 hours of salt fog exposure (right).

Corrosion Sensing Coating through Fluorescent Change

A commercially available solvent-based 3 part acrylic-urethane clear coating was used for testing. Fluorescein containing microparticles were incorporated into the coating at 0.05% by weight; the coating was then drawn down onto 3" x 2" R type Q-Panels. After cured, the coated panels were then taped to the bottom of polystyrene well plates and scribed at the center of the panel. A baseline reading was taken for all panels using the TECAN M1000® infinite fluorescence spectrometer before exposure to salt solution. After the initial reading was taken, approximately 50 mL of 5% aqueous sodium chloride (NaCl) solution was added to the well plates (sufficient to cover the entire panel) and the plates were sealed and placed back into the spectrometer. The parameters used for the fluorescence spectrometer are provided in Table 2.

All samples were scanned every 15 minutes. After the measurements were completed; the panels were removed and rinsed with deionized (DI) water and photographed. The resulting panels were further examined using a Keyence VHX-600® digital microscope at 100X magnification to correlate areas of high fluorescence intensity with corrosion spots on the panels observed visually and via fluorescence spectroscopy.

Table 2. Fluorescence Spectroscopy Instrument Parameters

Device	Tecan Infinite M1000 Pro
Plate	1536 Flat Bottom Transparent Polystyrene Well Plate
Mode	Fluorescence Top Reading
Excitation Wavelength	494 nm
Emission Wavelength	525 nm
Excitation Bandwidth	5 nm
Emission Bandwidth	5 nm
Gain	100 Manual
Flash Frequency	400 Hz
Integration Time	20 μ s
Lag Time	0 μ s
Settle Time	100 ms
Z-Position (Manual)	20000 μ m

A Zeiss LSM 710® confocal fluorescent microscope was also used to observe the test panels before and after salt immersion exposure. The following figures (Figure 5-7) show these images. These images show the fluorescein particle distribution in the coating before the salt water exposure, and the fluorescence intensity next to the corrosion sites (near the scribe area). While the 2D image confirms the local fluorescent indication signal, the 3D images reveals the intense fluorescent emission from the coating/metal interface where local pH changes directly correlate with metal hydroxide formation, the onset of corrosion process.

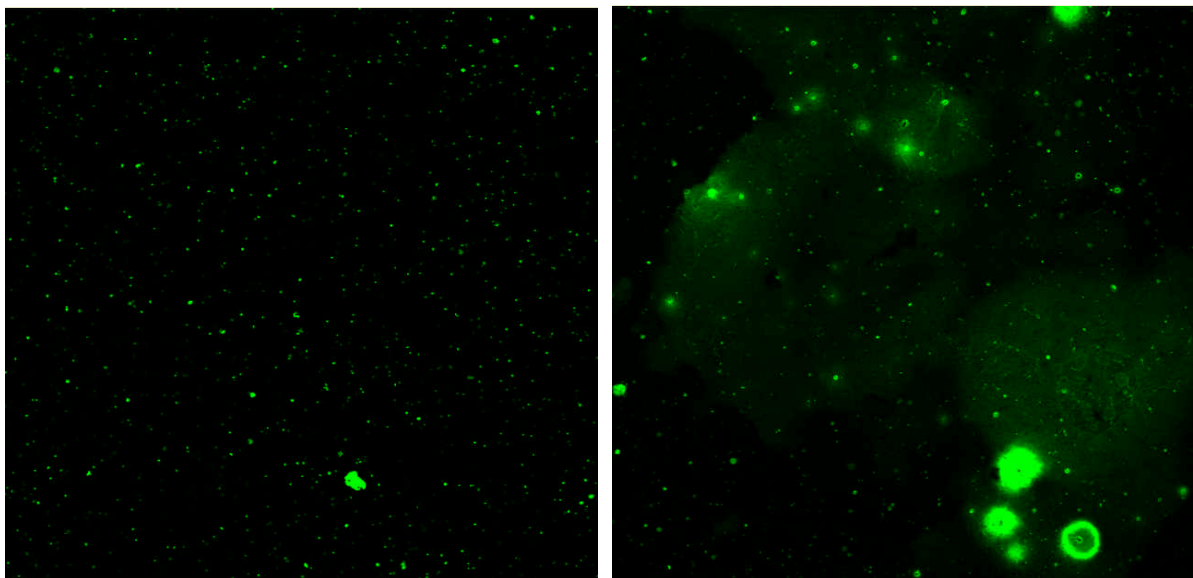


Figure 5. Confocal scanning laser microscopy 2D images (488 nm) of fluorescent corrosion sensing coating applied to cold rolled steel. On the left, unexposed panel; on the right, near scribe after 15 hours of immersion in 5% NaCl.

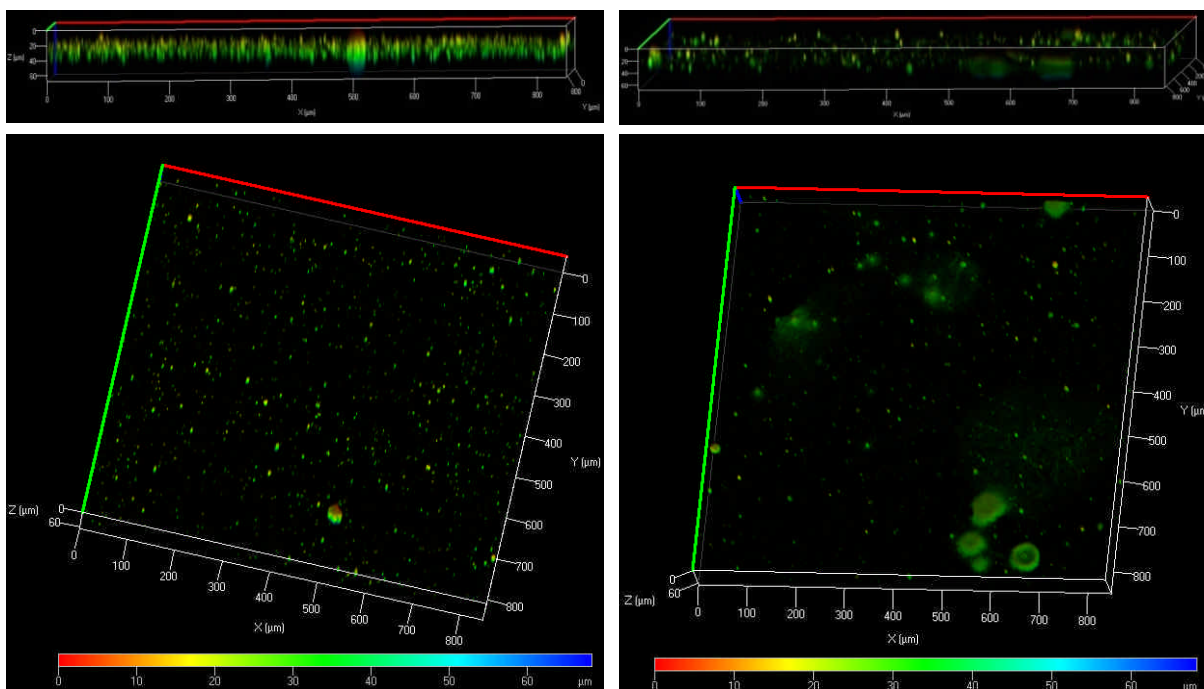


Figure 6. Confocal scanning laser microscopy 3D images (488 nm) of fluorescent corrosion sensing coating applied to cold rolled steel. On the left, unexposed panel; on the right, near scribe after 15 hours of immersion in 5% NaCl.

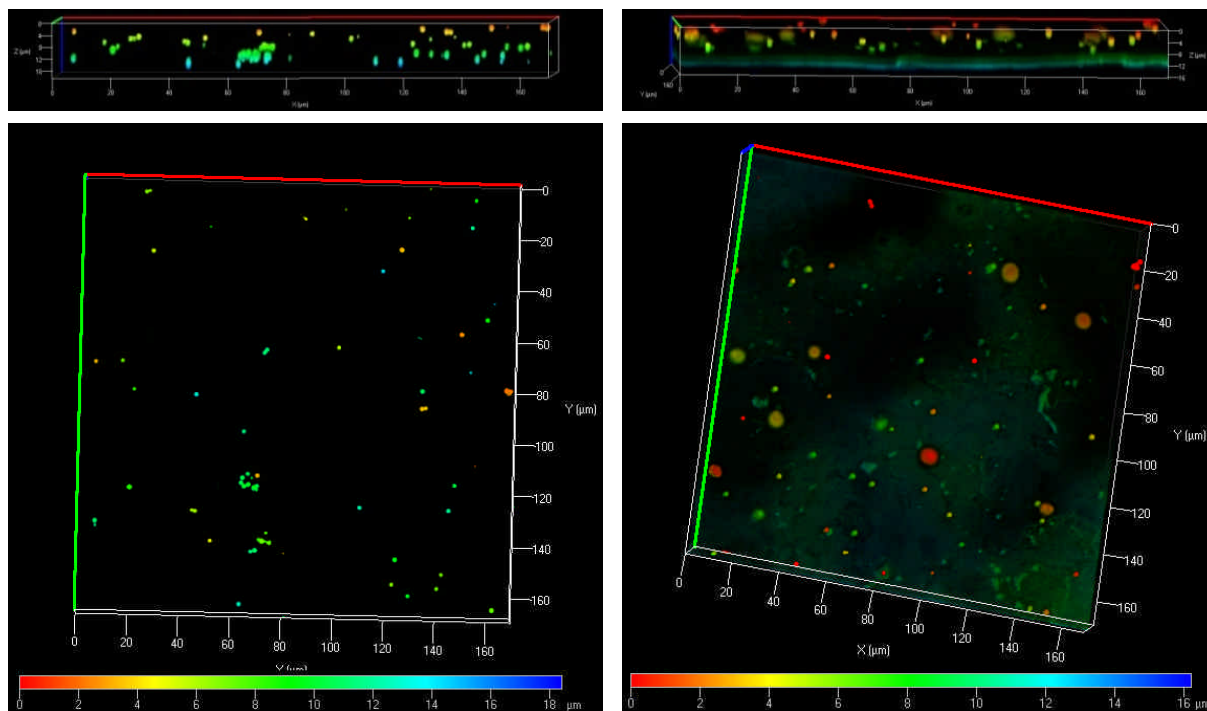


Figure 7. Confocal scanning laser microscopy 3D images (488 nm) of fluorescent corrosion sensing coating applied to cold rolled steel. On the left, unexposed panel; on the right, near scribe after 15 hours of immersion in 5% NaCl. zoomed in.

Figure 8 summarizes the TECAN reflectance fluorescence spectroscopy scanning composite image on the coated cold rolled steel panel during salt immersion exposure up to 5.5 hours, with an artificial defect in the middle. While the main event is at the defect sites, there are many other corrosion events occurring as early as 1 hour.

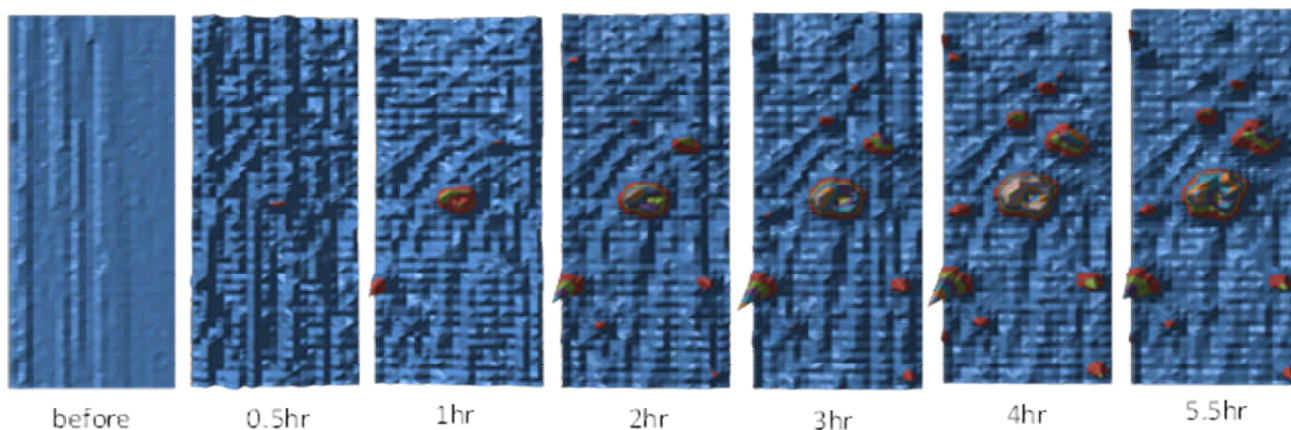


Figure 8. TECAN scan images show local corrosion events.

Figure 9 shows that after 15 hours of salt water immersion testing, the only visible corrosion to the unaided eye is at the induced defect point at the middle of the panel (picture on the left), while the fluorescence scanning images show many more early corrosion activity sites (middle); Optical microscope images at 100X magnification reveal very small corrosion spots corresponding to some of the corrosion events detected by the TECAN scanning method (optical microscopy images at right).

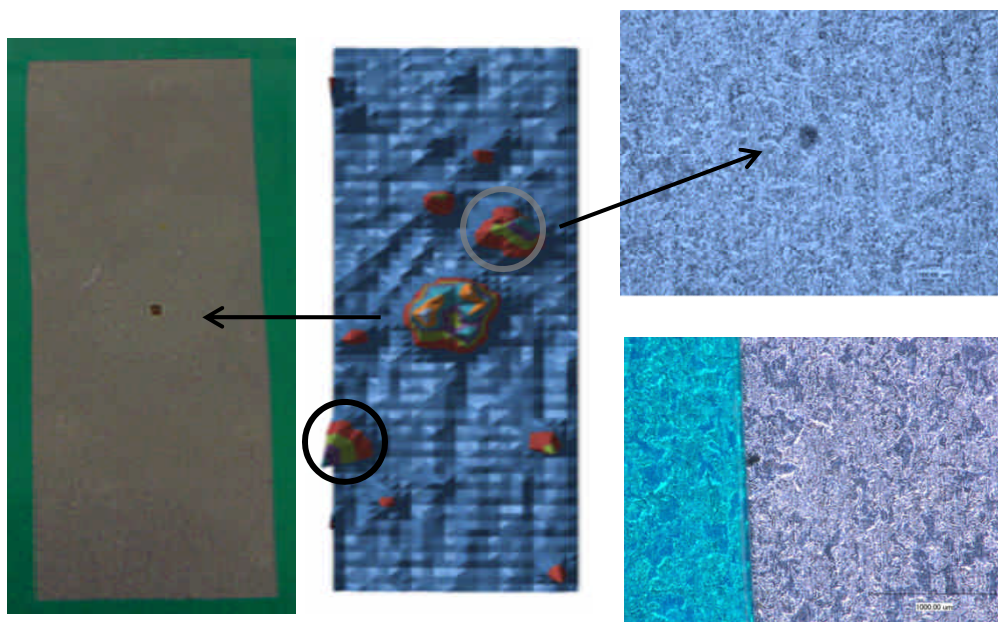


Figure 9. Fluorescent corrosion sensing coating for early corrosion detection. TECAN scan image after 5.5 hours salt water immersion testing is in the middle, while a picture and optical microscopy images (100X) of the panel after 15 hours of salt water immersion testing are on the left and right.

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